Risk Based Corrosion Chemistry Control

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Outline

- Current chemistry control program
- Initiative for broader chemistry control - Pitting
  - Lower hydroxide requirement
  - Lower nitrite requirement
- Probability based nitrite requirement
  - Statistical test matrix
  - Scoping testing
- Benefits

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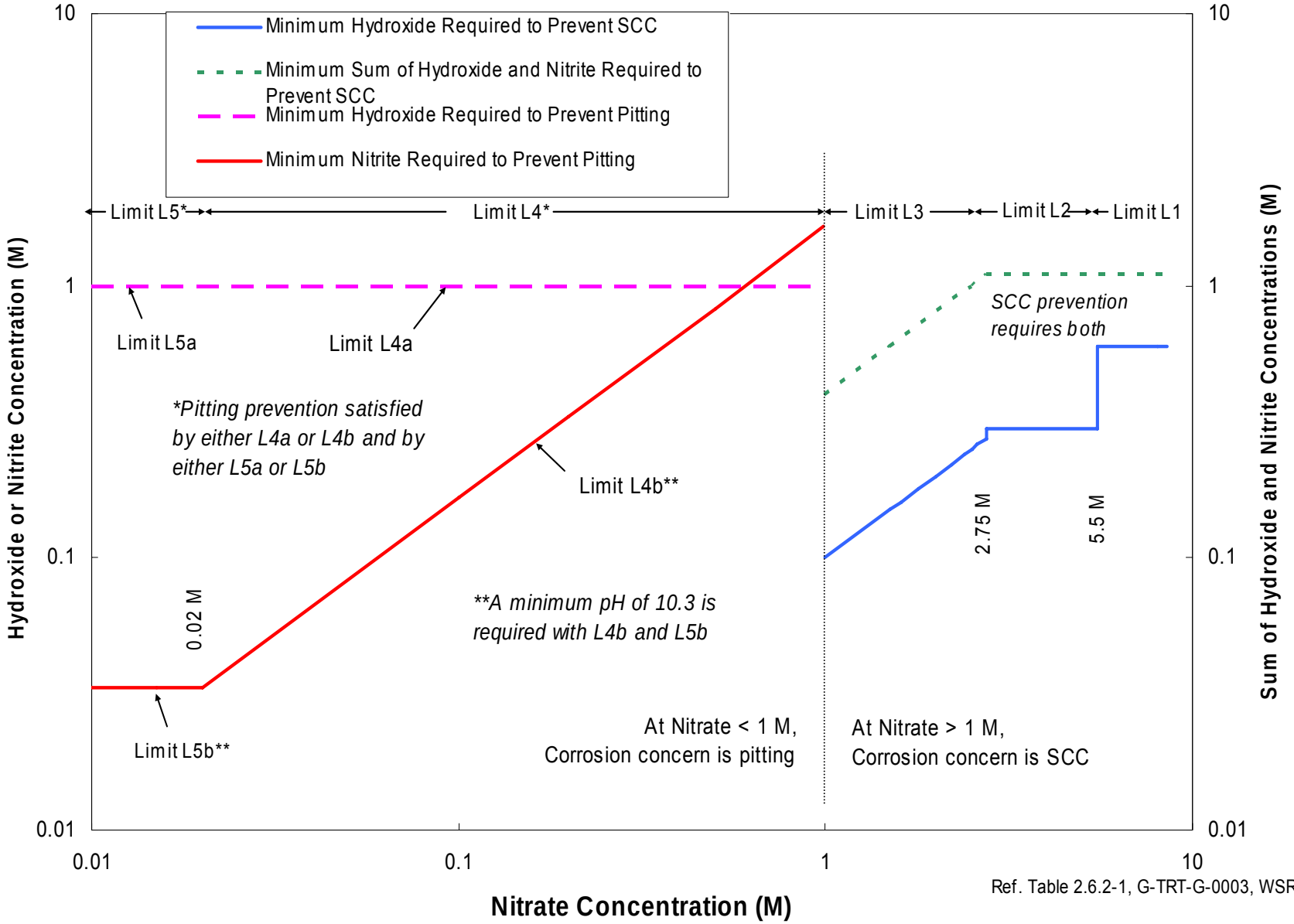
Chemistry Control Program



Ref. Table 2.6.2-1, G-TRT-G-0003, WSRC

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Broader Chemistry Control Initiative

- Chemistry control program intended to prevent pitting for $[NO_3^-] < 1M$
- Requirements
  - $[OH^-]_{min} = 1M$
  - $[NO_2^-]$ minimum
- Option 1: Lower hydroxide requirements
- **Option 2: Lower nitrite requirements**
  - **Probabilistic basis for pitting control with nitrite**

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Initial Predictive Statistical Models

- Logistic Regression
  - Binary Outcome

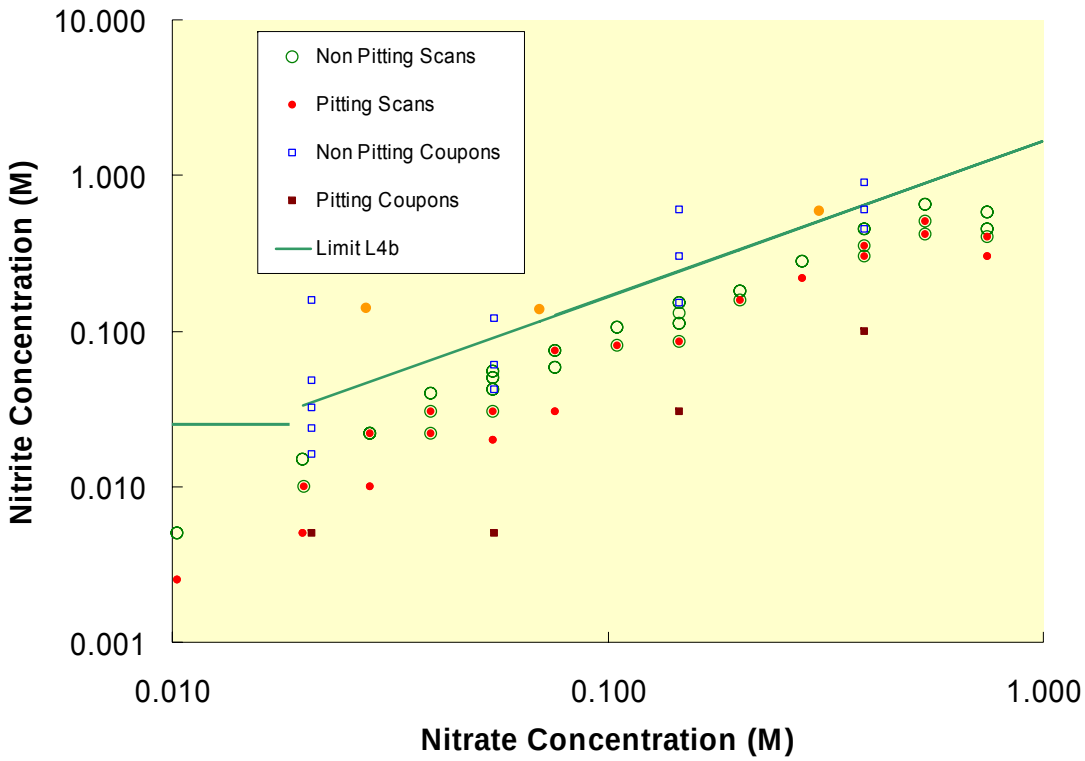
$P(x_1,x_2,T)=1/[1+\exp(B_0+B_1x_1+B_2x_2+B_3T)]$

- $x_1=\log[NO_3^-]$
- $x_2=\log[NO_2^-]$
- T= Temperature (°C)

- Artificial Neural Network
  - Training set + Test Set

- *Concluded that "chemistry control program could be relaxed without significantly affecting risk of pitting"*

- Cyclic polarization scans
- Coupon immersion testing



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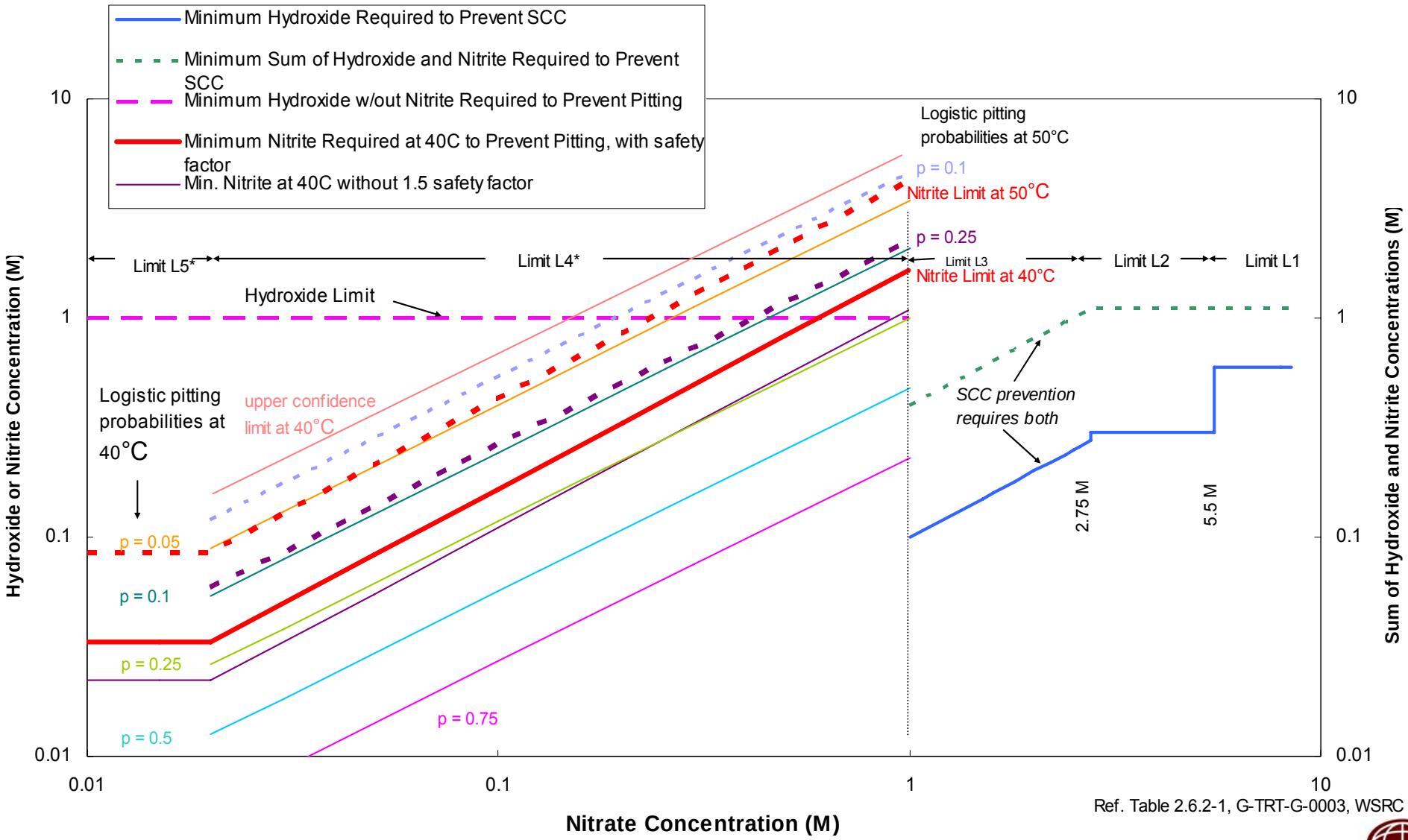
Regression and ANN Results



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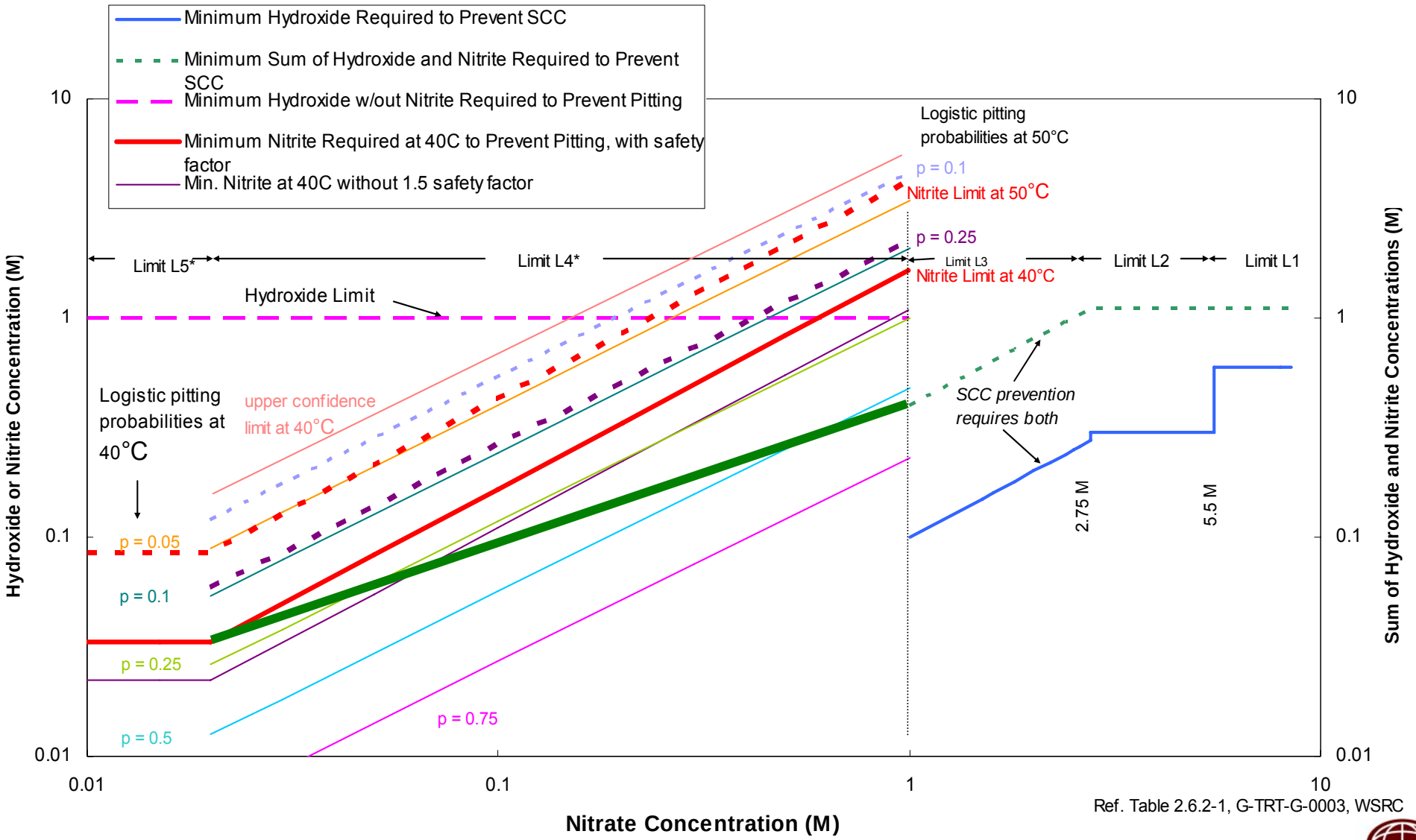
Example Lower Requirements



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Development of Statistical Basis

- Investigate the molar nitrite concentration to confidently inhibit pitting
- Initial scoping test matrix based upon data available

- Design space of $0.02M \leq [NO_3^-] \leq 1M$
  - Limit to 40°C

- Logistic regression
  - Binary outcome
  - Assuming pitting to occur at greater than 50% probability

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Models Considered

- Model 1: Initial Model

  $g(x_1,x_2)=1/[1+\exp(\beta_0+\beta_1 x_1+\beta_2 x_2)]$

  - $x_1=\log[NO_3^-]$
  - $x_2=\log[NO_2^-]$

- Model 2: Simplified as a mixture framework – Critical ratio

  $g(x_1,x_2) = \beta_1 x_1+\beta_2 x_2$

  - $x_1=\log[NO_3^-]$
  - $x_2=\log[NO_2^-]$
  - $x_1 + x_2 = 1$

- Model 3: Add total moles variable

  $g(x_1,x_2) = \beta_1 x_1+\beta_2 x_2+A(\beta_3 x_1+\beta_4 x_2)$

  - $x_1=\log[NO_3^-]$
  - $x_2=\log[NO_2^-]$
  - $x_1 + x_2 = 1$

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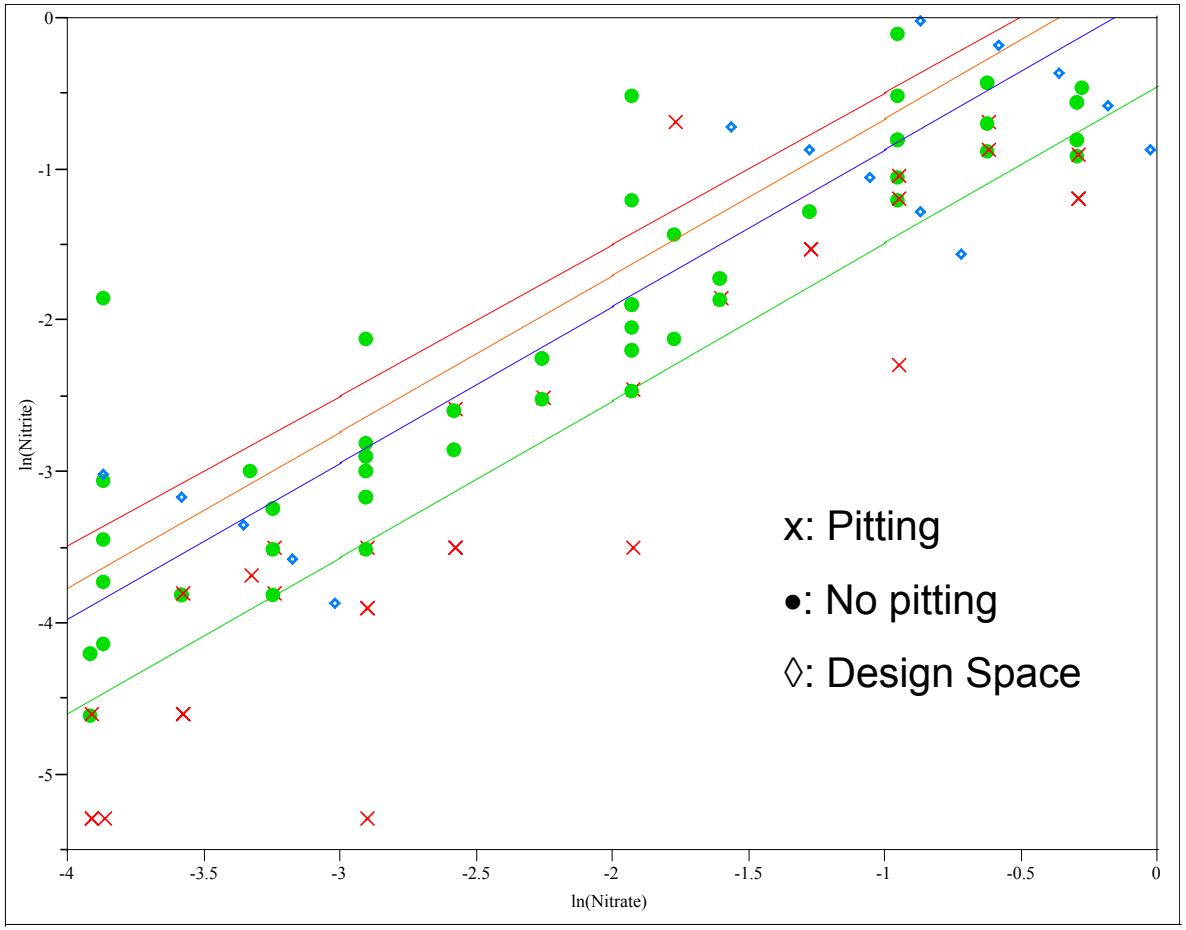
Design of Scoping Test Matrix

- Current chemistry control program
  - Nitrite = 1.66·nitrate
  - Probability of pitting is approximately 0.02 (or the odds of not pitting versus pitting are ~ 98%/2%) over the design space of interest.
- Scoping Test Matrix
  - Allows for investigation of amount/mixture models
  - Provides data over the entire design space of interest (i.e. higher nitrate)



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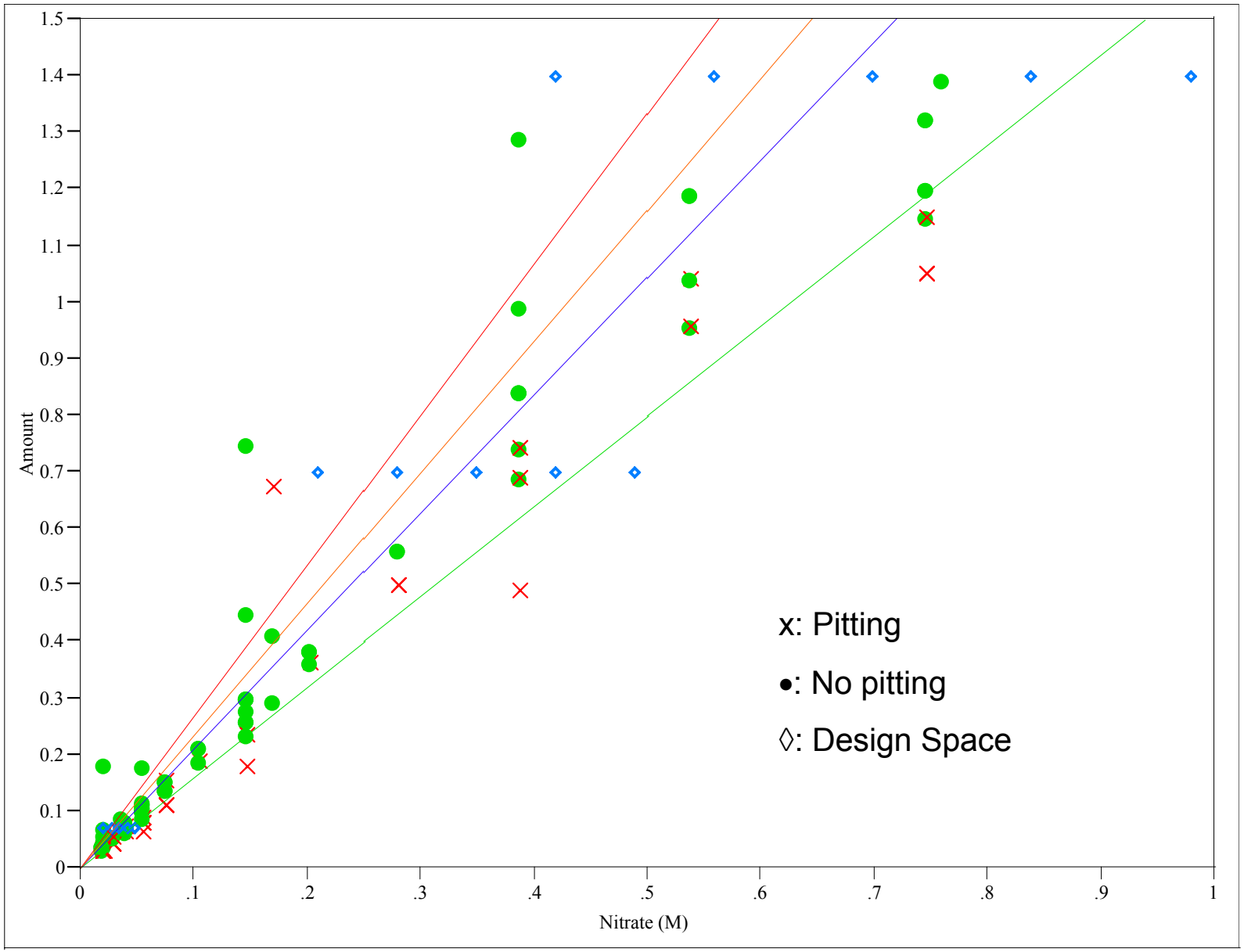
Design of Scoping of Test Matrix



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Model Predictions

		Model 1		Model 2		Model 3	
Nitrate (M)	Nitrite (M)	Prob(Pitting)	Likely Outcome	Prob(Pitting)	Likely Outcome	Prob(Pitting)	Likely Outcome
0.049	0.021	0.736	Pitted	0.753	Pitted	0.824	Pitted
0.042	0.028	0.361	Not Pitted	0.402	Not Pitted	0.400	Not Pitted
0.035	0.035	0.115	Not Pitted	0.129	Not Pitted	0.087	Not Pitted
0.028	0.042	0.029	Not Pitted	0.032	Not Pitted	0.013	Not Pitted
0.021	0.049	0.006	Not Pitted	0.007	Not Pitted	0.002	Not Pitted
0.49	0.21	0.789	Pitted	0.753	Pitted	0.686	Pitted
0.42	0.28	0.431	Not Pitted	0.402	Not Pitted	0.391	Not Pitted
0.35	0.35	0.149	Not Pitted	0.129	Not Pitted	0.158	Not Pitted
0.28	0.42	0.038	Not Pitted	0.032	Not Pitted	0.052	Not Pitted
0.21	0.49	0.008	Not Pitted	0.007	Not Pitted	0.016	Not Pitted
0.98	0.42	0.803	Pitted	0.753	Pitted	0.483	Not Pitted
0.84	0.56	0.453	Not Pitted	0.402	Not Pitted	0.380	Not Pitted
0.7	0.7	0.160	Not Pitted	0.129	Not Pitted	0.287	Not Pitted
0.56	0.84	0.042	Not Pitted	0.032	Not Pitted	0.209	Not Pitted
0.42	0.98	0.009	Not Pitted	0.007	Not Pitted	0.148	Not Pitted

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Experimentation

- Scoping test matrix design
  - Complement available data
  - Select and develop the appropriate, representative statistical model
  - Complete test matrix developed
- Cyclic polarization testing on scoping matrix completed
  - Accelerated electrochemical method to determine pitting susceptibility
  - Testing done with carbonate/bicarbonate additions to maintain pH at 10.7
  - Results indicate no pitting

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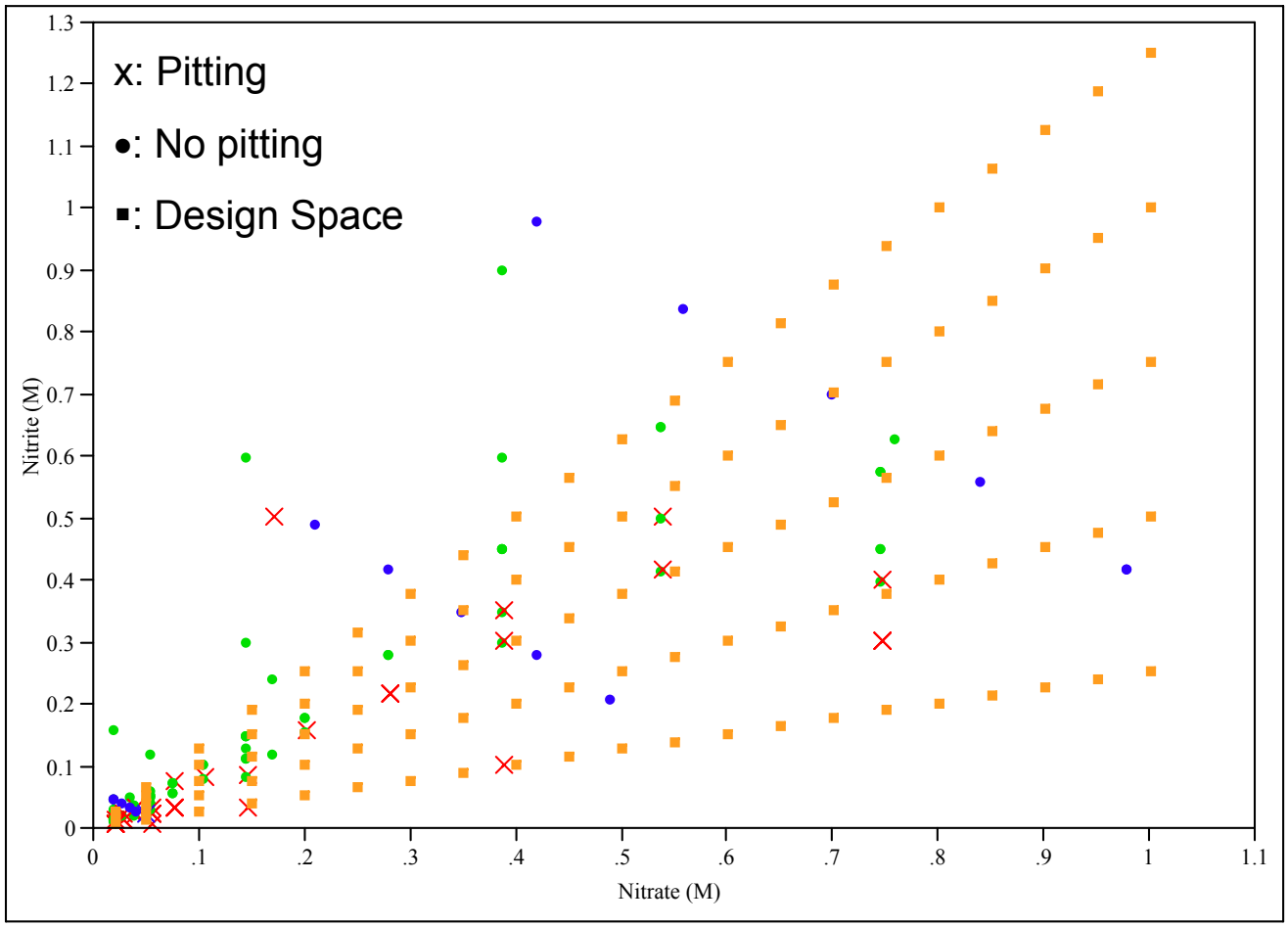
Complete Test Matrix



- 105 test points
- Multiple tests at each design point
- Coupon and electrochemical testing
- Addition of chlorides/sulfates
- Testing ongoing

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Summary/Conclusion

- Probabilistic approach to chemistry control initiative
- Preliminary experimental results indicate proof-of-concept
- Significant benefits
  - Reduces unnecessary conservatism in support of tank closure goals
  - Quantifies risk of pitting associated with particular chemistries
  - Maximum savings of tank space and cost of maintaining unnecessarily conservative chemistry control measures
  - Allows for tank specific risk acceptance

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